Effect of Gas Pressure on the Solubility and Diffusion of Polybutadiene in Polystyrene

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ABSTRACT: Tracer diffusion of 3000 g/mol perdeuterated polybutadiene (dPB) into high molecular weight polystyrene (PS) was measured with forward recoil spectroscopy (FRES) in the temperature range from 90 to 110 °C in the presence of argon and helium pressures up to 11.3 MPa. The diffusion coefficient for dPB in PS at 107 °C increases from 1.2×10^{-13} to 8.7×10^{-13} cm^2/s as the argon pressure is increased from atmospheric pressure to 11.3 MPa. When helium is the pressurizing medium, the diffusion coefficient for dPB in PS at 107 °C decreases from 1.2×10^{-13} to 3.7×10^{-14} cm^2/s as the pressure is increased from atmospheric pressure to 11.3 MPa. The results are explained in the framework of competing hydrostatic pressure and plasticization effects. The solubility of dPB in PS is independent of pressure, irrespective of the gas used as the pressurizing medium.

Introduction

The tracer diffusion of large molecules in polymers provides a sensitive probe of the dynamics of the polymer matrix. For example, the tracer diffusion coefficient (D) of 3000 g/mol perdeuterated polybutadiene (dPB) in polystyrene (PS) varies over 2 orders of magnitude in the temperature range from 96 to 115 °C.[1] The values of D as well as the apparent activation energy for the diffusion in this range near the PS glass transition temperature compare favorably to tracer diffusion measurements of photoreactive dye molecules in PS at the same temperatures.[2,3] In all of these experiments, the diffusion is coupled to the dynamics of the PS matrix, and small changes in temperature in this range result in large differences in matrix mobility and thus large variations in the measured diffusion coefficient.

Above the glass transition temperature, the temperature dependence of the diffusion coefficient is usually well described by a WLF equation in which the relationship between D and the temperature difference $T_{\text{experiment}} - T_g$ is readily apparent. Conditions which increase T_g decrease matrix mobility and decrease D, and those which decrease T_g increase mobility and increase D. The effect of hydrostatic pressure is to increase T_g.[4] However, some gases at high pressure are sufficiently soluble in PS so that they can act as plasticizers and lower T_g. Wang et al.[5] described the reduction in T_g of PS as a function of carbon dioxide pressure. They found that T_g went through a minimum near 20 MPa of CO_2 pressure and explained their results in terms of the competing effects of hydrostatic pressure and plasticization. This same framework of competing hydrostatic pressure and plasticization effects should be relevant to the behavior of the diffusion coefficient of dPB in PS in the presence of helium or argon gas pressure. On the other hand, neither hydrostatic pressure nor dissolved gas is expected to change the equilibrium solubility of dPB in PS as we will clarify below. Experiments were performed to examine the validity of these presumptions.

Experimental Section

Polymers. The polystyrene used in this study was supplied by Polysar (M_w = 350 000, M_n = 170 000). Perdeuterated polybutadiene (dPB) was synthesized in our laboratory via homogeneous anionic polymerization in benzene using *n*-butyllithium initiator. The perdeuterated butadiene was obtained from Cambridge Isotope Laboratories and purified as described by Cheng.[6] The molecular weight was 3000 and the polydispersity was 1.04 based on size-exclusion chromatography and an in-line viscometer. Deuterium NMR experiments showed that the microstructure of the dPB was 12% 1,2 and 88% 1,4-cis and -trans addition. With the exception of the *n*-butyl and proton end groups, the polymer is greater than 97% deuterated based on proton NMR results.

Sample Preparation. All samples were prepared in a similar manner. A piece of silicon wafer was washed in distilled water to remove any dust particles, rinsed with high-purity ethanol, and dried by spinning at 3000 rpm in air. A polystyrene layer was deposited on the wafer in a spin-coating process with solutions of PS in toluene. The samples were annealed in a vacuum oven for at least 8 h at approximately 100 °C to remove any residual solvent and to relax stresses caused by the spin-coating process. The objective was to create a bilayer sample consisting of dPB on top of the PS. We were unable to form a coherent film with the low molecular weight dPB. Instead heterogeneous films of dPB and PS were employed successfully as in our previous work.[1] These films were made by spin-coating solutions of blends of dPB and PS in toluene in which the PS accounted for 30–40% of the total polymer by weight. Thus, the dPB/PS blend layer was spun onto a glass slide, floated onto the surface of a water bath, and picked up with a PS-coated wafer. Each sample was dried in a vessel with a nitrogen purge at room temperature for at least 12 h. Care was taken in each preparation step to minimize the exposure of the dPB to oxygen, UV light, and heat to reduce the possibility of cross-linking.

The samples were heated in a brass sample chamber which was connected to a gas cylinder. The chamber was evacuated and back-filled with argon or helium, and the pressure was maintained constant with a regulator. The pressure was read from the gauge of the regulator with an accuracy of 50 kPa. The maximum pressure attainable was 11.3 MPa. In each experiment, the sample and chamber were immersed in an oil bath at a given temperature for a specific period of time. In this way the sample temperature reached 90% of its final steady-state value after 80 s and 99% after 180 s. The temperature of the bath itself dropped approximately 0.6 °C immediately after insertion of the sample chamber and regained a steady-state value (±0.1 °C) after approximately 2 min. The error in reported temperature is greater for those samples which were treated for short time periods. The minimum time period used in these experiments was 15 min. Each sample was quenched to room temperature to "freeze" the concentration versus depth profile for subsequent analysis, and then the gas pressure was released.

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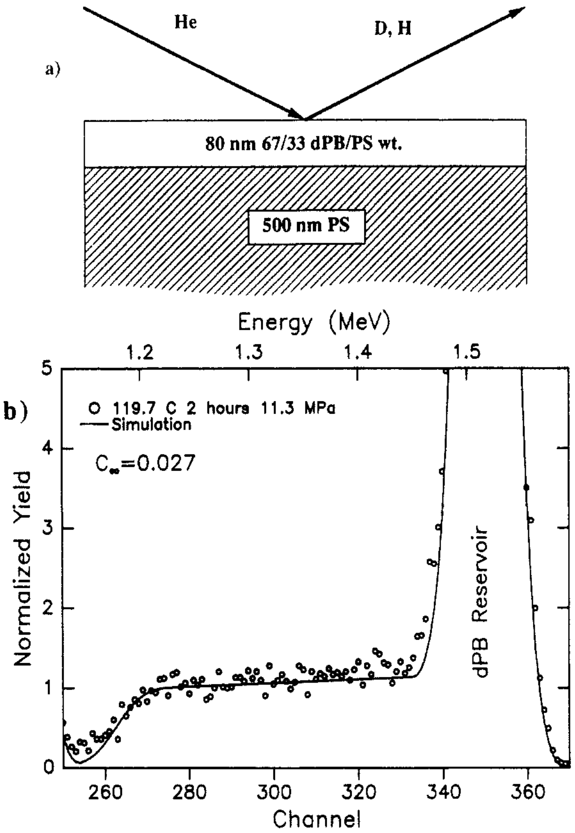

Figure 1. (a) Schematic of a typical sample in the solubility experiments. (b) FRES data and simulation for a sample held for 2 h at 119.7 °C with 11.3 MPa of argon. The solubility of dPB in PS in this sample is 0.027 volume fraction.

Forward Recoil Spectroscopy. All of the samples were analyzed with forward recoil spectroscopy (FRES) at the Cambridge Accelerator for Materials Science at Harvard University to determine concentration versus depth profiles of dPB in PS. This technique allows direct measurement of the diffusion profile of the deuterated species in the hydrogenated matrix for penetration depths in the range of 500 nm. Given this depth and a 5-min minimum experimental time period for accurate temperature control, the largest diffusion coefficient that can be measured is approximately 10^{-12} cm^2/s. Details of this technique and the data analysis are described elsewhere.[1,7-9]

Results and Discussion

Solubility limits and diffusion coefficients were determined from the FRES results with the aid of the RUMP software package developed for Rutherford Backscattering and FRES data analysis at Cornell University.[10,11] The software was purchased from Computer Graphics Service in Lansing, NY. This program performs complex iterative simulations of FRES data given the specific parameters of the experimental configuration and the physical and chemical characteristics of the species in the sample description.

Solubility Experiments. Some of the samples were held at temperatures of 106.7, 119.7, and 159.0 °C and gas pressures of either atmospheric pressure or 11.3 MPa for time periods of 1–24 h. The dPB/PS blend layer in these samples was approximately 80-nm thick and was 67% dPB and 33% PS by weight, and the pure PS substrate layer was approximately 500-nm thick. A schematic of a typical sample for the solubility experiments is shown in Figure 1a. The amount of dPB present is more than enough to saturate the PS substrate layer in the present experiment in the temperature range studied. Figure 1b shows the FRES data for a representative sample held at 119.7 °C for 2 h under 11.3 MPa of argon pressure. The normalized yield is proportional to the concentration of dPB, and the depth in the sample increases as the energy or channel number decreases. The dPB has diffused from the thin blended reservoir layer on the surface (1.47–1.56 MeV) into the initially homogenous PS layer, and the relatively flat concentration profile (1.22–1.44 MeV) indicates that the sample has reached equilibrium. The back edge of the sample corresponds to an energy of approximately 1.18 MeV. The solid line through the data is the best fit of a simulation to the data in which the concentration of dPB is assumed to be constant in the PS layer. For this sample, the solubility limit of dPB in PS, C_∞, is determined to be 0.027 volume fraction.

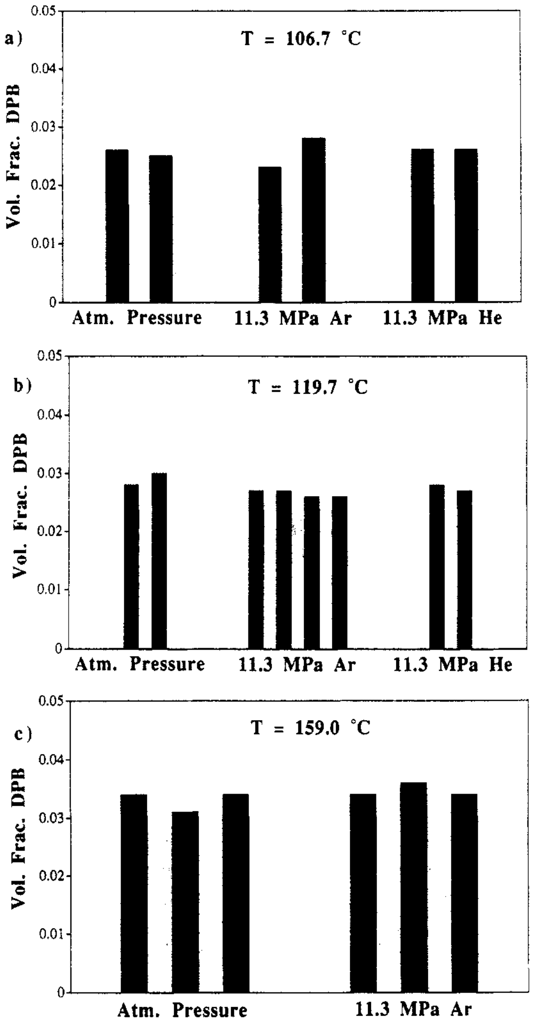

Figure 2. Solubility of dPB in PS determined from a number of different samples at (a) 106.7, (b) 119.7, and (c) 159.0 °C.

Figure 2 shows the solubility of dPB in PS determined from the FRES data for a number of different samples. The samples in parts a–c of Figure 2 were held at 106.7, 119.7, and 159.0 °C, respectively, at atmospheric pressure and at 11.3 MPa of gas pressure. Because the error in the solubility values is approximately 10%, there is no meaningful effect of either helium or argon gas pressure on the solubility of dPB in PS in the temperature range of the experiments. The observed absence of any effect of pressure on the solubility of dPB in PS can be predicted from a thermodynamic analysis which is presented in the appendix.

Diffusion Experiments. Other samples were held at temperatures ranging from 115.2 to 89.0 °C for time periods of 15–1020 min. with helium or argon gas pressure ranging from atmospheric pressure to 11.3 MPa. In these experiments the dPB/PS blend layer was approximately 35-nm thick and was 59% dPB and 41% PS by weight. The pure PS substrate layer was approximately 4-μm (4000-nm)

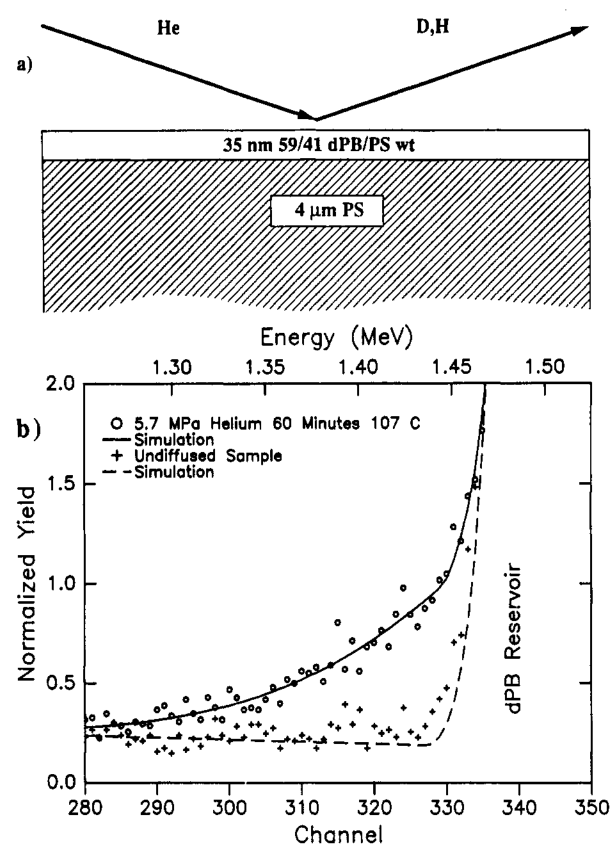

Figure 3. (a) Schematic of a typical sample in the diffusion experiments. (b) FRES data and simulations for an undiffused sample and for a sample held for 60 min at 107 °C with 5.7 MPa of helium pressure. The best fit to FRES data for the diffused sample is found with $C_\infty = 0.035$ and $D = 5.5 \times 10^{-14}$ cm^2/s.

thick. A schematic of a typical sample in the diffusion experiments is shown in Figure 3a. Diffusion times were chosen to obtain concentration profiles which would go to zero in penetration depths of order 200 nm. Figure 3b shows a representative sample which was held at 107.0 °C for 60 min at 5.7 MPa of helium pressure compared to an undiffused sample. The location of the interface between the thin blended reservoir layer of dPB on the surface and the initially homogeneous PS layer corresponds to a recoiled deuterium energy of approximately 1.46 MeV. Deuterium which recoils at energies below 1.46 MeV results from dPB which has diffused into the PS; the lower the energy, the deeper the dPB has diffused into the sample. The normalized yield is proportional to the concentration of dPB.[1] The dPB has clearly penetrated into the initially homogeneous PS layer. The solid lines through the data are best fits based on simulated samples for the two spectra. The undiffused sample is simulated as the bilayer structure depicted in Figure 3a. The consistent nonzero value for the counts of deuterium in the range of energy between the deuterium and hydrogen peaks, for example, the data at energies below 1.43 MeV in the undiffused sample in Figure 3b is representative of all the samples and is accounted for as pile-up. These counts are attributed to events when two particles of lower energy reach the detector at the same time and are counted as one single higher energy particle. For the diffused sample, the simulation of the data assumes that the diffusion profile of dPB in the PS layer is consistent with Fickian diffusion of a species diffusing into a half-space from a constant concentration at the interface. The constant concentration in this case is the equilibrium solubility limit, C_∞, of the dPB in PS at the temperature of the experiment. The concentration profile is given by[12]

$$C(x,t) = C_\infty \operatorname{erfc}[x/(4Dt)^{1/2}] \qquad (1)$$

where x is the depth of penetration, D is the diffusion coefficient, and t is time. The diffusion coefficients reported here are the values obtained from the best fits to the data using C_∞ and D as adjustable parameters. Another approach is to set C_∞ equal to the value determined in the solubility experiments at the temperature of interest and use only D as an adjustable parameter. Both methods result in consistent and equivalent values of D within the error of the FRES experiment as discussed in detail in our previous work.[1]

Figure 4a shows fits to the FRES data from samples which were held at 107.0 °C for 60 min at 0.8, 5.7, and 11.3 MPa of helium pressure. The dPB has clearly penetrated further into the initially homogeneous PS layer at the lower pressure for the case of helium. Figure 4b shows fits to the FRES data for samples which were held at 107.0 °C for 30 min at atmospheric pressure, 2.9, 5.7, and 11.3 MPa of argon pressure. In these samples the penetration of the dPB in the PS layer increases with increased argon pressure, the opposite of the effect of the helium pressure.

Figure 5 shows the effect of both helium and argon gas pressure on the diffusion coefficient for dPB in PS at a constant temperature of 107 °C. As the argon pressure is increased from atmospheric pressure to 11.3 MPa, D increases from 1×10^{-13} to 1×10^{-12} cm^2/s. Conversely, as the helium pressure is increased from atmospheric pressure to 11.3 MPa, D decreases from 1×10^{-13} to 4×10^{-14} cm^2/s. The explanation for this behavior is the difference in solubility between argon and helium in PS. The diffusion coefficient for dPB in PS is dictated by the mobility of the PS matrix in these experiments. The effect of hydrostatic pressure is to increase T_g, decrease mobility, and decrease D. Helium is effectively insoluble in PS, even at the higher pressures, and a decrease in D with increasing hydrostatic pressure is observed. Argon, however, is much more soluble in PS than helium. As the argon pressure is increased, the concentration of argon in PS increases and the PS becomes significantly plasticized. The plasticization decreases T_g, increases mobility, and increases D. When argon is the pressurizing medium, both the hydrostatic pressure effect to decrease D and the plasticization effect to increase D are present, and in the pressure range from atmospheric pressure to 11.3 MPa, the plasticization effect dominates. As described in the Introduction, Wang et al[5] separated these two effects in a framework to describe a minimum in T_g as a function of CO_2 pressure at approximately 20 MPa. Similarly, the diffusion coefficient for dPB in PS is expected to go through a maximum as T_g goes through a minimum at an argon pressure greater than the 11.3 MPa upper limit of our experimental setup.

Diffusion coefficients were also determined as a function of temperature at 11.3 MPa of helium pressure, atmospheric pressure,[1] and 11.3 MPa of argon pressure. These values are plotted in Figure 6a versus 1000/T. As mentioned in the Introduction, the temperature dependence of D above the glass transition temperature is usually well described by a WLF equation which can account for curvature in the data. However, our data do not span a large enough range to merit a fit beyond an Arrhenius equation with a temperature-independent activation energy. The apparent activation energy, ΔE, is found for each data set from the best least-squares fit of an Arrhenius equation to each set of data. The values of ΔE (Figure 6b) for the diffusion at 11.3 MPa of helium, atmospheric pressure, and 11.3 MPa of argon are 103, 99, and 96 kcal/mol, respectively. If the lowest temperature point (89 °C)

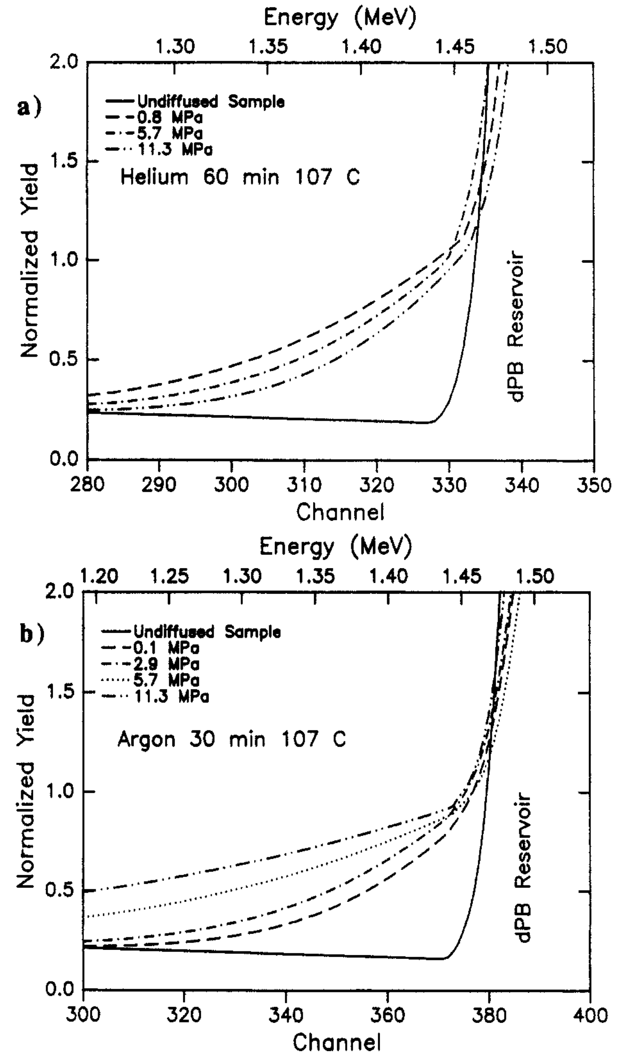

Figure 4. Best fits to FRES data for samples held at 107 °C with (a) various helium pressures for 60 min and (b) various argon pressures for 30 min.

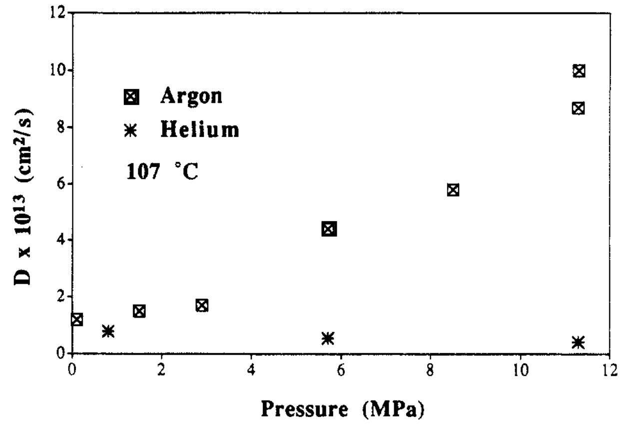

Figure 5. Plot of the diffusion coefficients determined from samples held at 107 °C with different argon and helium gas pressures vs pressure.

for the diffusion at 11.3 MPa of argon is omitted, ΔE is 81.3 kcal/mol, and r^2 improves from 0.965 to 0.989 in the Arrhenius fit. The concentration of helium and argon in PS is a function of temperature as well as pressure. The fact that the ΔE values are the same for the case of helium at 11.3 MPa and the case of atmospheric pressure is expected because in these experiments the concentration of gas in the PS is negligible in the entire temperature and pressure range studied. At 11.3 MPa of argon pressure, however, the lower apparent activation energy is due to the increase in the concentration of argon in PS associated with the decrease in temperature. Thus the degree of plasticization increases with decreasing temperature. Similarly, Wang et al.[5] described enhanced plasticization of PS at lower temperatures with isobaric CO_2 pressure.

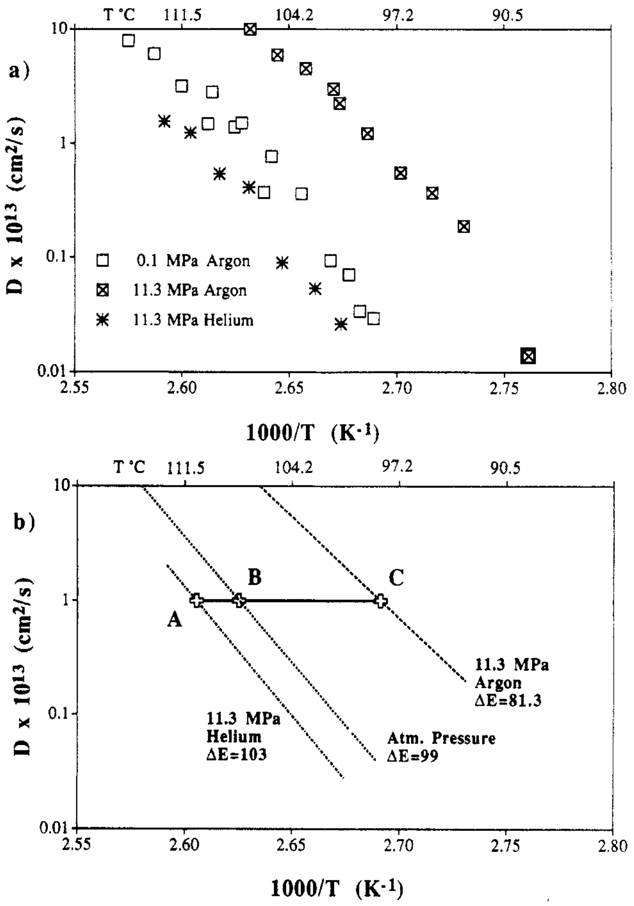

Figure 6. (a) Semilog plot of D vs $1000/T$ for samples with 11.3 MPa of helium pressure, atmospheric pressure, and 11.3 MPa of argon pressure. (b) Best fits of Arrhenius equations to the data. The solid line is drawn for $D = 1 \times 10^{-13}$ cm^2/s, and the labeled crosses mark the intersection of this line with the Arrhenius fits.

The diffusion coefficients found at 11.3 MPa of helium, atmospheric pressure, and 11.3 MPa argon can also be used to estimate the shift in T_g produced by the hydrostatic pressure effect as well as by plasticization in the temperature range of the experiments. Either gas at atmospheric pressure, and helium at higher pressures, is considered effectively insoluble in PS. The upward shift in T_g produced by 11.3 MPa of hydrostatic pressure is determined from the increase in temperature required to obtain the same diffusion coefficient for a sample held at 11.3 MPa of helium compared to a sample held at atmospheric pressure. This temperature difference can be found from the points where the solid line drawn in Figure 6b at a constant value of $D = 1 \times 10^{-13}$ cm^2/s intersects the Arrhenius fits to the diffusion coefficient data for the samples held at 11.3 MPa of helium and atmospheric pressure (segment $\overline{AB}$ in Figure 6b). The upward shift in T_g produced by 11.3 MPa of hydrostatic pressure is about 3 °C, which leads to a value of $\Delta T_g/\Delta P = 0.27$ °C/MPa. This value agrees well with $dT_g/dP = 0.30$ °C/MPa reported by Gee.[4] The downward shift in T_g produced by dissolved argon acting as a plasticizer is determined from the temperature decrease required to obtain the same diffusion coefficient for a sample held at 11.3 MPa of argon compared to a sample held at 11.3 MPa of helium. This temperature difference is found from segment $\overline{AC}$ in Figure 6b. This downward shift in T_g produced by argon plasticization at this pressure and temperature is 12 °C.

The diffusion coefficient for dPB in PS is a sensitive probe of the mobility of the PS matrix into which it is penetrating. The experiments at 11.3 MPa of helium show that pressure or negative mean normal stress increases T_g and decreases D. It is probable that positive mean normal stress (triaxial tension) increases D and decreases T_g. During the tensile deformation of blends of a few volume percent low molecular weight polybutadiene (PB) and polystyrene at room temperature, the PB locally diffuses into PS in the neighborhood of crazes where the PS is under significant positive mean normal stress.[13,14] An estimate for the diffusion coefficient for the PB in the PS craze material is 3×10^{-12} cm^2/s,[1] the same order of magnitude as the diffusion coefficients found near the glass transition temperature of PS in this study. If the PB molecule is acting as a probe of PS matrix dynamics, then the deforming PS in the vicinity of a craze, at room temperature but under large positive mean normal stress, is as mobile as unstressed PS at much higher temperatures.

Summary

The solubility of 3000 g/mol perdeuterated polybutadiene in polystyrene is not a function of helium or argon gas pressure within the error of our experiments. The diffusion coefficient for dPB in PS was found to be a sensitive probe of PS mobility. D decreased with increasing helium pressure because the effectively insoluble helium acts only to produce hydrostatic pressure which is known to increase T_g and decrease PS mobility. $\Delta T_g/\Delta P$ found from the diffusion coefficient data agreed well with the value of $\mathrm{d}T_g/\mathrm{d}P$ reported by Gee[4] in this pressure range. D increased with increasing argon pressure because of plasticization effects. The concentration of dissolved argon in PS increases with pressure from atmospheric pressure to 11.3 MPa, and the resulting plasticization dominates the hydrostatic pressure effect to decrease T_g, increase PS mobility, and increase D.

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Appendix

We are considering a case in which the molecular weights of the polymers are very different. We have observed that the low molecular weight polybutadiene (PB) is somewhat soluble in the high molecular weight PS and the solubility of the PS in the PB is negligible. We may then address the expected influence of pressure on solubility by considering a thermodynamic system at constant temperature in which PS, saturated with the low molecular weight PB, is in equilibrium with a reservoir of PB. At equilibrium, the chemical potential of the pure PB in the reservoir, $\mu_{\mathrm{PB}}^{\mathrm{pure}}$, must be equal to $\mu_{\mathrm{PB}}^{\mathrm{blend}}$, the chemical potential of the PB dissolved in the PS. These two quantities depend on pressure as follows:[15]

$$\mu_{\mathrm{PB}}^{\mathrm{pure}} - \mu_{\mathrm{PB}}^{\mathrm{ref}} = \mathrm{P}\mathrm{V}_{\mathrm{PB}} \qquad \text{(A1)}$$

$$\mu_{\mathrm{PB}}^{\mathrm{blend}} - \mu_{\mathrm{PB}}^{\mathrm{ref}} = \mathrm{RT}\ln[\gamma C_\infty] + P\bar{V}_{\mathrm{PB}} \qquad \text{(A2)}$$

where $\mu_{\mathrm{PB}}^{\mathrm{ref}}$ is the chemical potential of pure PB at $P = 0$ and temperature T, V_{PB} is the molar volume, $\bar{V}$ is the partial molar volume, γ is an activity coefficient, and C_∞ is the volume fraction of PB in PS at equilibrium. V_{PB}, $\bar{V}_{\mathrm{PB}}$, and γ may be considered to be functions of pressure.

The most general case would be to consider that the PB reservoir pressure, P^{res}, and the pressure on the blend, P^{blend}, are not identical so that

$$RT\ln[\gamma C_\infty] + P^{\mathrm{blend}}\bar{V}_{\mathrm{PB}} = P^{\mathrm{res}}V_{\mathrm{PB}} \qquad \text{(A3)}$$

Using eq A3 it is possible to compare the equilibrium solubility of PB in PS for two different conditions of pressure as follows:

$$\psi = \frac{C_\infty(P=P_2)}{C_\infty(P=P_1)} = \frac{\gamma_1}{\gamma_2} \exp\left[\frac{P_2^{\mathrm{res}}V_{\mathrm{PB},2} - P_1^{\mathrm{res}}V_{\mathrm{PB},1} - P_2^{\mathrm{blend}}\bar{V}_{\mathrm{PB},2} + P_1^{\mathrm{blend}}\bar{V}_{\mathrm{PB},1}}{RT}\right] \qquad \text{(A4)}$$

Several interesting cases can be analyzed from eq A4, but the most relevant here is $P_i^{\mathrm{res}} = P_i^{\mathrm{blend}}$ for $i = 1,2$ which leads to the observation that the solubility ratio, ψ, differs from unity only if the blend is nonideal:

$$\psi = \frac{\gamma_1}{\gamma_2}\exp\left[\frac{P_2(V_{\mathrm{PB},2} - \bar{V}_{\mathrm{PB},2}) - P_1(V_{\mathrm{PB},1} - \bar{V}_{\mathrm{PB},1})}{RT}\right] \qquad \text{(A5)}$$

If, for example, $V_{\mathrm{PB},2}$ is larger than $\bar{V}_{\mathrm{PB},2}$ by 10% for 3000 g/mol PB, $P_2 = 11.3$ MPa, $P_1 = 0$, $T = 100$ °C, and the ratio of the activity coefficients is unity, then $\psi = 1.09$. If the system is ideal, the molar volumes are identical to the partial molar volumes and the activity coefficients are unity so that $\psi_{\mathrm{ideal}} = 1$, and solubility is independent of pressure. To the extent that the nonidealities for our PB/PS system are expected to be rather small (C_∞ is on the order of 0.04 volume fraction, compressibilities are low,[16] and the maxium pressure achieved was on the order of 10 MPa (100 atm)), it is reasonable that we observed no measurable pressure dependence of C_∞ in this study.

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